Portable Elemental Analysis Device for Real-Time Chemical Analysis of Aluminium

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Abstract

The operation of aluminium reduction cells relies on frequent sampling and chemical analysis. The sampling and analysis process is time-consuming and carries the risk of introducing measurement errors related to sample preparation and handling. This paper presents a portable device that uses Liquid Phase Laser-Induced Breakdown Spectroscopy (LP-LIBS) to analyze liquid metal composition down to below 10 ppm in a matter of seconds. In routine operation, the full cycle time for obtaining the chemical composition from a series of cells is below 90 seconds per cell. The correlations of analysis results with the conventional analysis method, spark optical emission spectroscopy (spark-OES), are also discussed. In addition to improving process control, monitoring the aluminium chemistry next to the cells also provides immediate results upon which operator can react to risk situations such as cathode failure/tap-outs. The potential offered by using machine learning and chemical analysis data to predict such failures is described.

Keywords: LIBS, Chemical analysis, Aluminium.

1. Introduction

The capital and operational costs of aluminium production are escalating, and cathode life contributes to one of the significant costs, where a cathode may cost more than $150 000 in materials and human resources [1]. The word cathode is used in the aluminium industry to describe the entire contents of the steel shell that contains the molten metal and the electrolyte. This includes the electrically conducting carbon lining with current collector bars, refractories, and insulation material. There are different contributing factors to the cathode life, but according to [2], the cathode itself contributes 50 %, while the other 50 % comes from operational procedures. Thus, improving the process by frequently monitoring the aluminium chemistry and avoiding cell leaks/tap-outs can significantly save cathode costs. Tap-outs usually start due to cracks or holes in the cathode lining that gradually reach out to the collector bars. If the cracks open, the molten aluminium begins to penetrate and fill the gap, which may initiate the cathode failure of the lining. The cathode failure can be a bottom failure (high Fe, high Cu tap-out through collector bars) or side failure (high Si, red side, side tap-out, SiC lining). Both types of failures are equally important [3]. The contamination of liquid aluminium by Fe, Si or Cu can give valuable information on materials problems, operational problems, bath ratio control, and cell heat balance. It can be particularly important when old cells are pushed to their limits with the line current. All plants record tap-outs and their causes, the most common being cell age. Cathode failures can also be accompanied by increased cathode voltage, overheated shell, cathode lining temperature, and contaminated aluminium. Such recorded data may be useful to track the operational parameters and materials and they are important to predict the future behavior of cells. Early prediction can help assist cell maintenance, such as plugging the hole or gap by flake alumina. The plugging of aluminium-infiltrated cracks is crucial. This helps avoid further damage and limit the extension of the cracks, which can be intensified by electromagnetic turbulence and chemical erosion.

The company DTE has been developing stationary and portable elemental analyzers for liquid aluminium, along with a machine-learning-based cloud platform (IREAS) that helps to maximize plant efficiencies, sustainability and cut emissions. DTE’s fully automated stationary analyzers have been tested in the industry, confirming that they are competitive with current laboratory analysis of process samples [4-7].

The portable DTE elemental analyzer discussed in this paper uses laser-induced breakdown spectroscopy (LIBS) to analyze the composition of the molten metal directly. LIBS is a spectroscopic technique that uses a high-energy laser pulse to generate a plasma on a sample surface and analyzes the spectral emissions from the generated plasma. LIBS can provide accurate, rapid, real-time multi-element detection for any type of material – solid, liquid, or gas [8-14]. It detects multiple chemical elements simultaneously, including light elements such as Li, B and Be. For many elements, detection limits of trace elements in the ppm range have been demonstrated in molten aluminium [4]. To date, however, the adoption of LIBS-based technologies in the industry has been limited and mainly focused on metal scrap sorting and identification with limited accuracy [11,15].

DTE supplies compact battery-powered analyzers, suitable for field measurements, thus creating the possibility for in-situ analysis of aluminium in reduction cells. The demand for in-situ analysis will only grow as industries drive their digital transformation towards integrating Industry 4.0. Within the aluminium industry, DTE’s analyzers supplement aluminium chemistry results with advanced analysis where the chemical data from liquid metal is used to alert the operator, not only about deviated measurements but also possible future cell tap-outs or anode failures.

This paper’s focus is on reporting the accuracy of DTE’s portable liquid metal analyzers by comparing its performance with the traditional spark-OES technique. The implications for the future of chemical analysis in the potroom will also be discussed.

2. LIBS Attributes and Comparison with Traditional Spark-OES Method

LIBS and OES are two different plasma emission techniques that can be used to analyze aluminium samples. As mentioned above, LIBS uses a laser pulse to generate the plasma, whereas spark-OES uses a high voltage pulse source to excite plasma between an electrode and the sample. Both methods analyze spectrally resolved light emission from the plasma. Laser excitation makes the LIBS technique suitable not only for solid samples but also for liquids and gas. DTE’s analyzers are specifically adapted to measure liquid metal as it gives numerous advantages over solid sample analysis. First, it helps to eliminate sample handling and sample preparation steps. These steps are tedious and may introduce measurement errors due to the segregation of elements or pores or cracks forming during pouring and solidification of the sample, contamination of samples from the molds or during preparation, and mix-up of samples. Second, eliminating the above steps also removes some of the safety hazard issues related to manual sample handling and transport. The third and most significant advantage is that it enables frequent real-time measurements with immediate feedback. This helps to deliver valuable intelligence through regular monitoring of impurity elements, thus improving cell operations. In contrast, conventional potroom samples are usually collected in sets and analyzed with some hours delay or more, depending on how loaded the laboratory is. Consequently, the condition of the cells can be very different from the conditions that analyzed samples represent and may no longer valid, especially for cells that are close to failure. Therefore, immediate chemical results can contribute to an improvement in cell operation as the response time is reduced from hours to seconds. A profitability analysis for real-time measurements in aluminium plants is discussed elsewhere in these proceedings [17].

3. Potroom Implementation

Operation of a portable liquid metal analyzer (EA-1000, DTE) at Century Aluminum (Grundartangi, Iceland) was reported previously [16]. The present paper presents results obtained using an upgraded version of this equipment that was used at Rio Tinto ISAL (Hafnafjordur, Iceland) over a period of three months (Figure 1). The analyzer is non-immersive and has no consumables, except for argon gas supplied from a 5 litre argon cylinder, and does not need daily calibration. In the current configuration, the battery life of the analyzer for regular operation was up to 6 h. The analyzer was transported between cells using an electrical vehicle, as shown in Figure 1, but the unit can also be mounted on a manually operated pushcart or a self-driving vehicle.

Aluminium samples were extracted from a number of different reduction cells, for a total of 900 unique LIBS measurements. After LIBS analysis of the liquid metal, a reference sample was cast from the analyzed melt sample using ASTM-standard molds for analysis at DTE’s laboratory (using a Thermo Scientific ARL iSpark 8820), while 900 additional solid samples were collected separately from the respective cells for automated spark-OES analysis at Rio Tinto ISAL (using a Thermo Scientific ARL iSpark 8860). The sampling sequence for the portable analyzer was illustrated previously [16]. The current device offers a similar measurement cycle time, as low as 70-90 seconds per cell in routine operation. This time includes extraction of a sample of liquid metal using a standard ladle and pouring into a second ladle clamped to the analyzer platform, the execution of the LIBS measurement, displaying results on-screen and filing to a database, and driving the vehicle to the next cell to be analyzed.

Figure 1. Portable elemental analyzer mounted on an electric vehicle (left). A liquid metal sample is extracted and poured into a ladle clamped to the analyzer platform (right).

The IREAS analysis platform included thresholds for Fe, Si, and Cu that were adopted for each cell, considering the history of chemical data of the cell. Furthermore, if the measurement results deviated considerably from the last measurements performed on the same cell, the device requests another measurement (see Figure 2) and, in some cases, a change of ladle, to avoid possible contamination from the sample extraction tools. If the measurement result is confirmed, the operator can immediately decide on a reaction on the plant floor.

Results of last measurement is suspicious and should be re-done

Start measurement for pot number 2003

Show results for pot 2001

Figure 2. An alarm from the device to repeat sampling due to suspicious measurements.

4. Results and Discussion

Although LIBS analysis can, in principle, determine the full set of trace elements in aluminium that are normally detected with the spark-OES method, this paper will focus on Fe, Si and Cu as these are the main elements that are monitored during metal tap-outs. Out of the 900 samples, 16 measurements were removed from the analysis due to apparent sample mix-ups. For illustrative purpose, a comparison between the OES at Rio Tinto ISAL versus in-situ LIBS results on the liquid metal, as well as OES results from DTE's laboratory (OES LAB), for measurements of 40 subsequent cell measurements is shown in Figure 3.

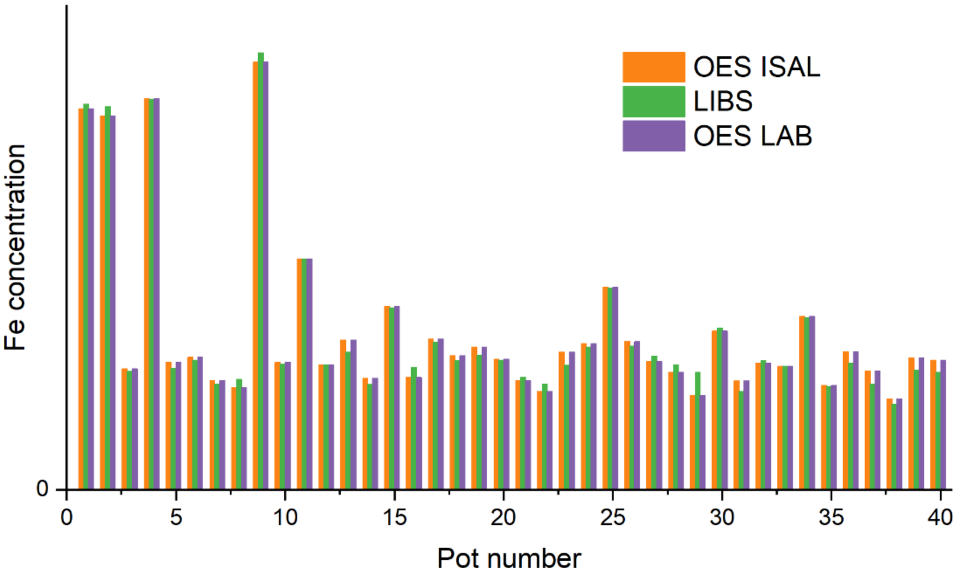

Figure 3. The relative concentration of Fe in different cells measured with three different analyzers.

For illustration, linear regression lines are shown for the case of Fe, for the OES at Rio Tinto ISAL versus in-situ LIBS results on the liquid metal, OES results from DTE's laboratory (OES LAB) versus LIBS analysis, and between the two spark-OES instruments (see Figure 4). The correlation coefficients (Pearson's R) were found to be 0.97, 0.989 and 0.985, respectively. The higher degree of correlation between LIBS and OES LAB is consistent with the fact that it involves the analysis of the same sample of extracted metal, while the OES at Rio Tinto ISAL involves analysis of separately extracted samples.

The measured difference between two measurements, e.g. $\Delta_{\text{OES LAB-LIBS}}=c_{\text{OES LAB}}-c_{\text{LIBS}}$, was calculated for all sets of measurements, for the different elements Fe, Si and Cu. The distributions are shown in Figure 5, including Gaussian fits to the data that confirms its normal distributions. The standard deviation of the fitted curves to the observed measurement differences in data sets of OES at Rio Tinto ISAL vs. LIBS, OES at LAB vs. LIBS and OES at Rio Tinto ISAL vs. OES LAB for Fe were 84 ppm, 73 ppm and 50 ppm, respectively. Assuming a typical value of standard deviation of the OES measurements of potroom samples of 1-2 %, it can be assumed that the variations between the two OES measurements is mainly related to the fact that the samples are extracted separately from the cells, thus representing, at least partly, an inherent uncertainty in the sampling (sample-to-sample variation). This is also consistent with wider distribution of differences in the case of comparison between LIBS analysis and Rio Tinto ISAL OES than for the comparison between the LIBS analysis and DTE's OES, also seen as an increased scatter in correlation curves 4a and 4c. The offset in the distribution curve from zero difference in the case of Fe reveals a systematic difference in the measurements of the two OES devices. For Si, the respective standard deviations of the distributions in Fig. 5 (second row) were found to be 29 ppm, 29 ppm and 22 ppm and for Cu (third row, where the concentration is considerably lower), they were 0.7 ppm, 0.8 ppm, and 0.6 ppm. The standard deviations for the distribution of differences in the case of Fe, Si, and Cu are similar to previously reported values using the EA-1000 portable elemental analyzer [16], where corresponding standard deviation values for LIBS-OES differences were also reported for Ga (13 ppm), Zn (5 ppm), Mg (13 ppm), Ni (10 ppm), Ti (7 ppm), Mn (6 ppm), and Cr (4 ppm), for concentration ranges associated with typical cell operation.

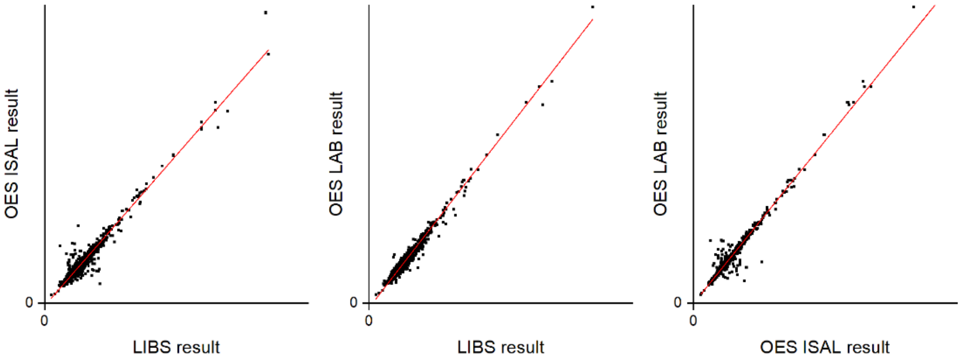

Figure 4. Linear regression plots for Fe analysis, comparing the different analysis methods.

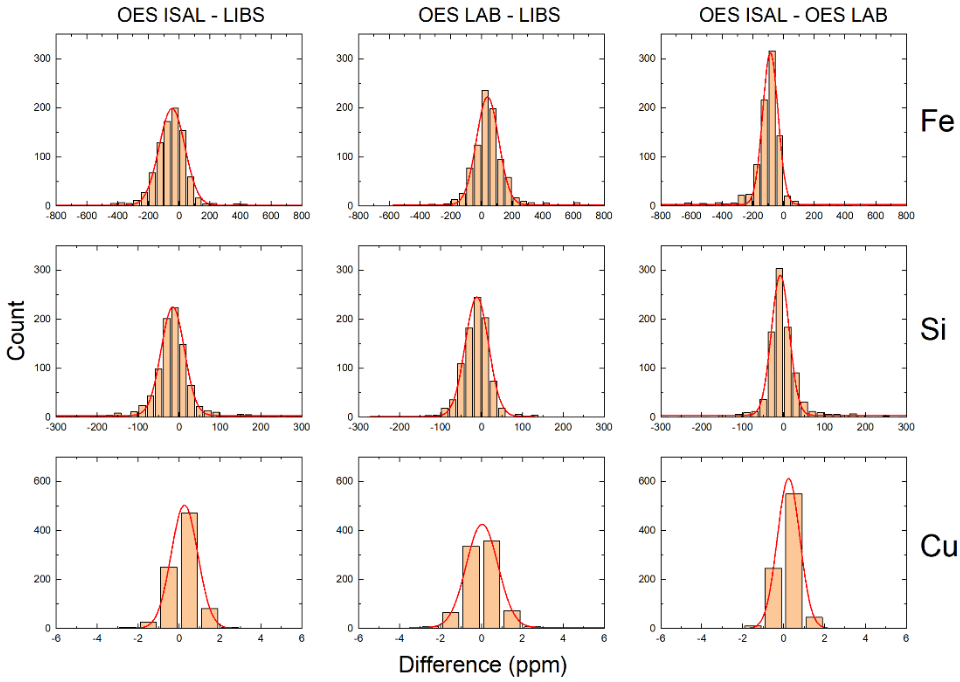

Figure 5. Distribution of differences between LIBS measurements on liquid metal and OES reference measurements from the laboratory and Rio Itinto ISAL for Fe, Si and Cu, as well as differences between the two OES analyzers. Solid red curves represent normal distribution curves fitted to the data.

5. Using Real-Time Concentration Measurements for Predictive Maintenance and Cathode Failure Prediction

As pointed out above, a clear advantage of real-time chemical analysis is the ability to analyze more frequently – and with immediate feedback – to execute predictive maintenance of the electrolysis cells and/or avoid cathode failures or sudden tap-outs. While some issues develop over long time periods (weeks or months), other changes appear more suddenly, even on timescales shorter than the typical cycle times for conventional analysis of solid potroom samples using centralized laboratory equipment. In order to establish the predictive power of chemical analysis to foresee serious events relating to cell degradation or failure, DTE and Rio Tinto ISAL have collaborated on analyzing 5-year historical potroom data, with the aim of constructing machine learning models for implementation in the IREAS platform. The data included the chemical composition of liquid aluminium in each cell and failure cases. To evaluate the model, the dataset was randomly divided into training and test sets (80/20).

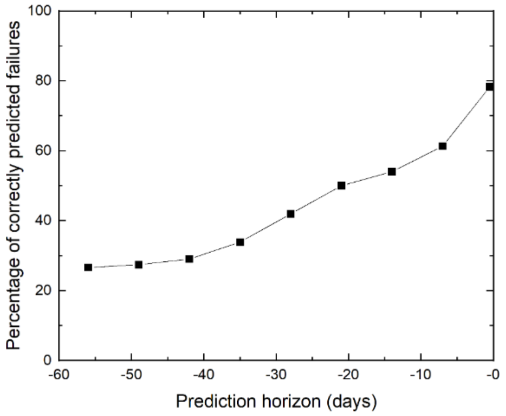

Figure 6. Cell failure prediction accuracy based on chemical analysis data.

As an initial step and using chemical analysis data alone, implementing logistic regression and random-forest methods, it was found that more than 25 % of cathode failures could be predicted with a 2-month time horizon, increasing to close to 80 % of cathode failures predicted with a 12-hour time horizon (see Figure 6). Prediction accuracy will be further improved by including additional physical data collected during cell operations, such as cell age, copper bar temperature, and other process variables that enhance prediction. Further details of the machine learning models and their implementation on real-time data will be presented elsewhere, including the correlation between different chemical species on one hand and failure modes and prediction horizons on the other.

6. Conclusion

DTE's portable elemental analyzer has been shown to deliver immediate chemical analysis of Fe, Si and Cu in molten aluminium from reduction cells, correlating well with OES analysis of conventionally extracted solid samples. Deployment of portable analyzers for potroom control hold great promise not only for real-time chemical analysis, but also as a predictive tool for potroom operation.

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